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The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy a certain number of requirements. Thus it must have no toxicological drawbacks, it must be able to give shades 35 of the desired intensity and it must be able to withstand external agents (light, bad weather, washing, permanent-waving, perspiration, rubbing).

The dyes must also be able to cover white hair and, lastly, they must be as unselective as possible, i.e. they must give the smallest possible colour

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide has the drawback of causing appreciable degradation of the fibres, as well as considerable bleaching of the keratin fibres, which is not always desirable.

It is known that the most common technique for obtaining a permanent reshaping of the hair consists, in a first stage, in opening the keratin -S-S-disulphide (cysteine) bonds using a composition containing a suitable reducing agent (reduction step) followed, after having rinsed the hair thus treated, by reconstituting, in a second stage, the said disulphide bonds by applying to the hair, which has been placed under tension beforehand (curlers and the like), an oxidizing composition (oxidation step, also known as the fixing

step) so as finally to give to the hair the desired shape. This technique thus makes it equally possible either to make the hair wavy or to straighten it or to remove its curliness. The new shape given to the hair by a chemical treatment such as above is remarkably long-lasting and in particular resists the action of washing with water or shampoos, as opposed to simple standard techniques for temporary reshaping, such as hairsetting.

The reducing compositions which may be used in order to carry out the first step of a permanent-waving operation generally contain, as reducing agents, sulphites, bisulphites, alkylphosphines or, preferably, thiols. Among the thiols, those commonly used are cysteine and the various derivatives thereof, cysteamine and the derivatives thereof, thiolactic acid or thioglycolic acid, the salts thereof and the esters thereof, in particular glyceryl thioglycolate.

As regards the oxidizing compositions needed to carry out the fixing step, use is usually made in practice of compositions based on aqueous hydrogen peroxide, sodium bromate or persalts such as sodium perborate, which have the drawback of being liable to damage the hair.

The problem of the technique of the permanent-waving operations known to date is that their application to the hair induces long-term adverse changes in the quality of the hair. The essential causes of these adverse changes in the quality of the hair are a reduction in its cosmetic properties, such as its sheen and its feel, and degradation of its mechanical properties, more particularly degradation of its mechanical strength due to swelling of the keratin fibres during the rinsing between the reduction step and the oxidation step, which can also be reflected by an increase in its porosity. The hair is weakened and can become brittle during subsequent treatments such as blow-drying.

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The same problem of adverse changes in keratin fibres is encountered during processes for bleaching the hair.

It is known that the permanent reshaping or  
5 bleaching of keratin fibres can also be carried out  
under milder conditions using oxidizing systems other  
than hydrogen peroxide, such as enzymatic systems.  
Thus, processes for the permanent reshaping or  
bleaching of keratin fibres have already been proposed,  
10 in particular in patent application EP-A-0,310,675,  
with compositions comprising an enzyme such as pyranose  
oxidase, glucose oxidase or uricase, in the presence of  
a donor for the said enzyme. Although being used under  
conditions which do not result in degradation of the  
15 keratin fibres which is comparable to that caused by  
conventional permanent-waving or bleaching processes,  
these oxidizing formulations nevertheless lead to  
results which are still insufficient, as regards the  
curl hold over time, as regards the compatibility of  
20 permanent-waved or bleached hair with subsequent  
treatments, as regards the degradation of the  
mechanical properties of the permanent-waved hair, in  
particular the reduction of the porosity of the hair,  
and as regards the reduction of the cosmetic properties  
25 such as the feel, or alternatively as regards the  
uniformity of the bleaching along the keratin fibres.

The aim of the present invention is to solve  
the problems mentioned above.

The Applicant has discovered, surprisingly,  
30 novel compositions containing, as oxidizing system, at  
least one enzyme of 2-electron oxidoreductase type in  
the presence of at least one donor for the said enzyme  
and at least one aminosilicone, which can constitute,  
in the presence of oxidation dye precursors (oxidation  
35 bases) and optionally couplers, ready-to-use dye  
formulations which lead to more homogeneous, more  
intense and more chromatic colorations without giving  
rise to any significant degradation, these colorations  
being relatively unselective and showing good

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(a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

The 2-electron oxidoreductase(s) used in the oxidizing compositions in accordance with the invention can be chosen in particular from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

10 By way of example, mention may be made in particular of uricase extracted from boar liver, uricase from *Arthrobacter globiformis*, as well as uricase from *Aspergillus flavus*.

The 2-electron oxidoreductase(s) in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition, and even more preferably from 0.1 to 5% by weight approximately relative to this weight.

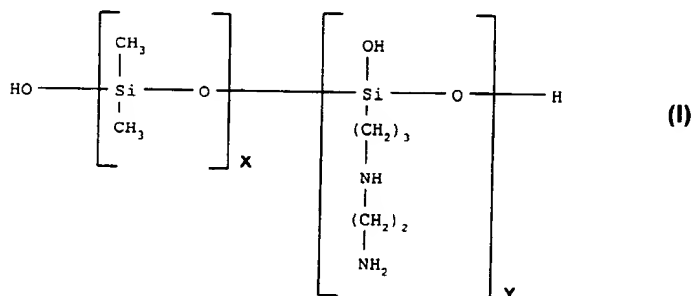
The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the 2-electron oxidoreductase used. For example, as donors for the pyranose oxidases, mention may be made of D-glucose, L-sorbose and D-xylose; as a donor for the glucose oxidases, mention may be made of D-glucose; as donors for the glycerol oxidases, mention may be made of glycerol and dihydroxyacetone; as donors for the lactate oxidases, mention may be made of lactic acid and its salts; as donors for the pyruvate oxidases, mention may be made of pyruvic acid and its salts; and

lastly, as donors for the uricases, mention may be made of uric acid and its salts.

The donor(s) (or substrate(s)) used in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition in accordance with the invention, and even more preferably from 0.1 to 5% approximately relative to this weight.

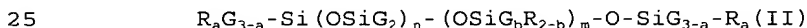
According to the invention, the term aminosilicone is understood to denote any silicone containing at least one primary, secondary or tertiary amine or a quaternary ammonium group. Mention may thus be made of:

(a) the polysiloxanes referred to in the CTFA dictionary as "amodimethicone" and corresponding to formula (I):



in which x and y are integers dependent on the molecular weight, generally such that the said number-average molecular weight is between 5000 and 500,000 approximately;

(b) cationic silicone polymers corresponding to the formula:



in which:







5

formula:



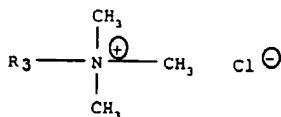
10

R<sub>1</sub> represents a monovalent hydrocarbon-based radical containing from 1 to 18 carbon atoms, and in particular

s represents an average statistical value from 20 to 200  
10 and in particular from 20 to 50.

One polymer belonging to this class is the polymer sold by the company Union Carbide under the name "Ucar Silicone ALE 56".

It is possible, for example, to use the product  
20 sold under the name "Cationic Emulsion DC 929" by the  
company Dow Corning, which comprises, besides  
amodimethicone, a cationic surfactant comprising a  
mixture of products corresponding to the formula:



Use may also be made, for example, of the product sold under the name "Cationic Emulsion DC 939" by the

company Dow Corning, which comprises, besides amodimethicone, a cationic surfactant which is trimethylcetylammonium chloride, in combination with a nonionic surfactant of formula  $C_{13}H_{27}-(OC_2H_4)_{12}-OH$ , known under the CTFA name "trideceth-12".

Another commercial product which can be used according to the invention is the product sold under the name "Dow Corning Q2 7224" by the company Dow Corning, containing, in combination, trimethyl-silylamodimethicone of formula (III) described above, a nonionic surfactant of formula:  $C_8H_{17}-C_6H_4-(OCH_2CH_2)_{40}-OH$ , known under the CTFA name "octoxynol-40", a second nonionic surfactant of formula:  $C_{12}H_{25}-(OCH_2-CH_2)_6-OH$ , known under the CTFA name "isolaureth-6", and propylene glycol.

The compositions in accordance with the invention contain the aminosilicones defined above at weight contents which can be between 0.05% and 10%, preferably between 0.1% and 5% and even more preferably between 0.2% and 3%, relative to the total weight of the composition.

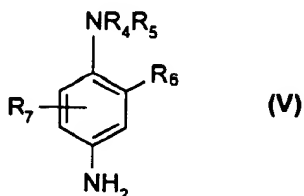
A subject of the present invention is also a ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, of the type comprising, in a medium which is suitable for dyeing, at least one oxidation base and, where appropriate, one or more couplers, which is characterized in that it contains:

- (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,
- (b) at least one aminosilicone.

The nature of the oxidation base(s) used in the ready-to-use dye composition is not a critical factor. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

Among the para-phenylenediamines which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in

particular of the compounds of formula (V) below, and the addition salts thereof with an acid:



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in which:

- $\text{R}_4$  represents a hydrogen atom, a  $\text{C}_1\text{-C}_4$  alkyl radical, a  $\text{C}_1\text{-C}_4$  monohydroxyalkyl radical, a  $\text{C}_2\text{-C}_4$  polyhydroxyalkyl radical, a  $(\text{C}_1\text{-C}_4)\text{alkoxy}(\text{C}_1\text{-C}_4)\text{alkyl}$  radical, a  $\text{C}_1\text{-C}_4$  alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;
- $\text{R}_5$  represents a hydrogen atom, a  $\text{C}_1\text{-C}_4$  alkyl radical, a  $\text{C}_1\text{-C}_4$  monohydroxyalkyl radical, a  $\text{C}_2\text{-C}_4$  polyhydroxyalkyl radical, a  $(\text{C}_1\text{-C}_4)\text{alkoxy}(\text{C}_1\text{-C}_4)\text{alkyl}$  radical or a  $\text{C}_1\text{-C}_4$  alkyl radical substituted with a nitrogenous group;
- $\text{R}_6$  represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a  $\text{C}_1\text{-C}_4$  alkyl radical, a  $\text{C}_1\text{-C}_4$  monohydroxyalkyl radical, a  $\text{C}_1\text{-C}_4$  hydroxyalkoxy radical, an acetylamino  $(\text{C}_1\text{-C}_4)\text{alkoxy}$  radical, a  $\text{C}_1\text{-C}_4$  mesylaminoalkoxy radical or a carbamoylamino  $(\text{C}_1\text{-C}_4)\text{alkoxy}$  radical,
- $\text{R}_7$  represents a hydrogen or halogen atom or a  $\text{C}_1\text{-C}_4$  alkyl radical.

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Among the nitrogenous groups of formula (V) above, mention may be made in particular of amino, mono  $(\text{C}_1\text{-C}_4)\text{alkylamino}$ , di  $(\text{C}_1\text{-C}_4)\text{alkylamino}$ , tri  $(\text{C}_1\text{-C}_4)\text{alkylamino}$ , monohydroxy  $(\text{C}_1\text{-C}_4)\text{alkylamino}$ , imidazolinium and ammonium radicals.

30

Among the para-phenylenediamines of formula (V)

above, mention may be made more particularly of para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis( $\beta$ -hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis( $\beta$ -hydroxyethyl)aniline, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl- $\beta$ -hydroxyethyl)-para-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine and N-( $\beta$ -methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

Among the para-phenylenediamines of formula (V) above, para-phenylenediamine, para-toluylenediamine, 2-isopropyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

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5           Among the double bases which can be used as  
oxidation bases in the dye compositions in accordance  
with the invention, mention may be made in particular of  
the compounds corresponding to formula (VI) below, and  
the addition salts thereof with an acid:

$$\left[ \begin{array}{c} \text{Z}_1 \\ | \\ \text{C}_6\text{H}_3(\text{R}_8)(\text{R}_{10})(\text{NR}_{12}\text{R}_{13}) \end{array} \right] - \text{Y} - \left[ \begin{array}{c} \text{Z}_2 \\ | \\ \text{C}_6\text{H}_3(\text{R}_{11})(\text{R}_9)(\text{NR}_{14}\text{R}_{15}) \end{array} \right] \quad (\text{VI})$$

15 - Z<sub>1</sub> and Z<sub>2</sub>, which may be identical or different, represent a hydroxyl or -NH<sub>2</sub> radical which may be substituted with a C<sub>1</sub>-C<sub>4</sub> alkyl radical or with a linker arm Y;

20 - the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C<sub>1</sub>-C<sub>6</sub> alkoxy radicals;

25 - R<sub>8</sub> and R<sub>9</sub> represent a hydrogen or halogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, a C<sub>2</sub>-C<sub>4</sub>

polyhydroxyalkyl radical, a C<sub>1</sub>-C<sub>4</sub> aminoalkyl radical or a linker arm Y;

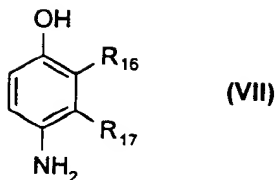
- R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub>, which may be identical or different, represent a hydrogen atom, a linker arm Y or  
5 a C<sub>1</sub>-C<sub>4</sub> alkyl radical;  
it being understood that the compounds of formula (VI) contain only one linker arm Y per molecule.

- Among the nitrogenous groups of formula (VI) above, mention may be made in particular of amino,  
10 mono(C<sub>1</sub>-C<sub>4</sub>)alkylamino, di(C<sub>1</sub>-C<sub>4</sub>)alkylamino, tri(C<sub>1</sub>-C<sub>4</sub>)alkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino, imidazolinium and ammonium radicals.

- Among the double bases of formula (VI) above, mention may be made more particularly of N,N'-bis(β-  
15 hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-  
20 N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

- Among these double bases of formula (VI), N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

- Among the para-aminophenols which can be used as  
30 oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (VII) below, and the addition salts thereof with an acid:



in which:

-  $R_{16}$  represents a hydrogen or halogen atom or a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyl,  $(C_1$ - $C_4$ )alkoxy( $C_1$ - $C_4$ )alkyl,  $C_1$ - $C_4$  aminoalkyl or hydroxy( $C_1$ - $C_4$ )alkylamino-( $C_1$ - $C_4$ )alkyl radical,

-  $R_{17}$  represents a hydrogen or halogen atom or a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyl,  $C_2$ - $C_4$  polyhydroxyalkyl,  $C_1$ - $C_4$  aminoalkyl,  $C_1$ - $C_4$  cyanoalkyl or  $(C_1$ - $C_4$ )alkoxy-( $C_1$ - $C_4$ )alkyl radical,

it being understood that at least one of the radicals  $R_{16}$  or  $R_{17}$  represents a hydrogen atom.

Among the para-aminophenols of formula (VII) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-( $\beta$ -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

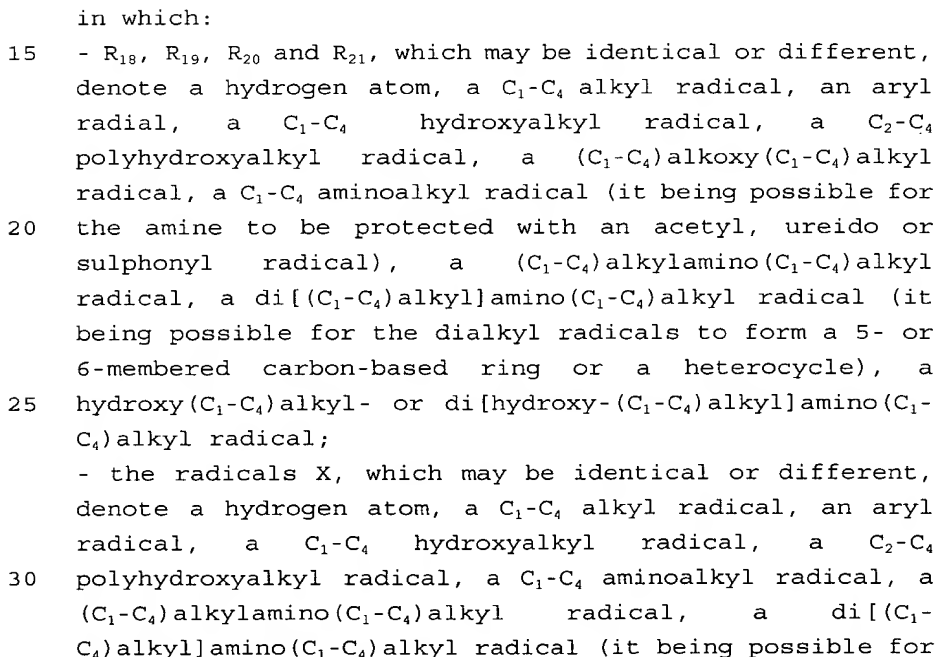
Among the heterocyclic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly



Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-( $\beta$ -methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

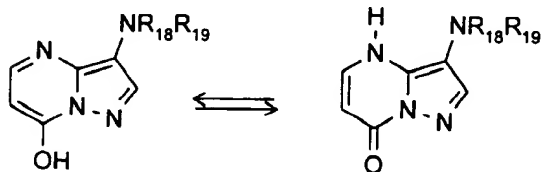
20 Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3,843,892, DE 4,133,957 and patent applications WO 94/08969, WO 94/08970, FR-A-2,733,749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-  
25 diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole,  
30 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,  
35 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-

5           Among the pyrazolopyrimidine derivatives, mention  
may be made more particularly of the pyrazolo[1,5-  
a]pyrimidines of formula (VIII) below, and the addition  
salts thereof with an acid or with a base and the  
tautomeric forms thereof, when a tautomeric equilibrium  
10 exists:



- the dialkyls to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl- or di[hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl]amino(C<sub>1</sub>-C<sub>4</sub>)alkyl radical, an amino radical, a (C<sub>1</sub>-C<sub>4</sub>)alkyl- or di[(C<sub>1</sub>-C<sub>4</sub>)alkyl]amino radical; a halogen atom, a carboxylic acid group or a sulphonic acid group;
- i is equal to 0, 1, 2 or 3;
  - p is equal to 0 or 1;
  - q is equal to 0 or 1;
  - n is equal to 0 or 1;
- with the proviso that:
- the sum p + q is other than 0;
  - when p + q is equal to 2, then n is equal to 0 and the groups NR<sub>18</sub>R<sub>19</sub> and NR<sub>20</sub>R<sub>21</sub> occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;
  - when p + q is equal to 1, then n is equal to 1 and the group NR<sub>18</sub>R<sub>19</sub> (or NR<sub>20</sub>R<sub>21</sub>) and the OH group occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions.

When the pyrazolo[1,5-a]pyrimidines of formula (VIII) above are such that they contain a hydroxyl group on one of the positions 2, 5 or 7 α to a nitrogen atom, a tautomeric equilibrium exists represented, for example, by the following scheme:



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- Among the pyrazolo[1,5-a]pyrimidines of formula (VIII) above, mention may be made in particular of:
- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
  - 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
  - pyrazolo[1,5-a]pyrimidine-3,5-diamine;
  - 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;

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- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
- 5 - 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol;
- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol;
- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 10 - 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

- 15       The pyrazolo[1,5-a]pyrimidines of formula (VIII) above can be prepared by cyclization starting with an aminopyrazole, according to the syntheses described in the following references:

- EP 628559 Beiersdorf-Lilly.
- 20 - R. Vishdu, H. Navedul, Indian J. Chem., 34b (6), 514, 1995.
- N.S. Ibrahim, K.U. Sadek, F.A. Abdel-Al, Arch. Pharm., 320, 240, 1987.
- R.H. Springer, M.B. Scholten, D.E. O'Brien,
- 25 T. Novinson, J.P. Miller, R.K. Robins, J. Med. Chem., 25, 235, 1982.
- T. Novinson, R.K. Robins, T.R. Matthews, J. Med. Chem., 20, 296, 1977.
- US 3907799 ICN Pharmaceuticals.

- 30       The pyrazolo[1,5-a]pyrimidines of formula (VIII) above can also be prepared by cyclization starting from hydrazine, according to the syntheses described in the following references:

- A. McKillop and R.J. Kobilecki, Heterocycles, 6(9),
- 35 1355, 1977.
- E. Alcade, J. De Mendoza, J.M. Marcia-Marquina, C. Almera, J. Elguero, J. Heterocyclic Chem., 11(3), 423, 1974.

- K. Saito, I. Hori, M. Higarashi, H. Midorikawa, Bull. Chem. Soc. Japan, 47(2), 476, 1974.

5 The oxidation base(s) in accordance with the invention preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

10 The couplers which can be used are those used conventionally in oxidation dye compositions, i.e. meta-phenylenediamines, meta-aminophenols and meta-diphenols, mono- or polyhydroxylated naphthalene derivatives, sesamol and its derivatives and heterocyclic compounds such as, for example, indole derivatives, indoline  
15 derivatives, benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo[3,2-d]oxazole derivatives, pyrazolo[3,4-d]thiazole derivatives, thiazoloazole  
20 S-oxide derivatives and thiazoloazole S,S-dioxide derivatives, and the addition salts thereof with an acid.

These couplers can be chosen in particular from 2-methyl-5-aminophenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-  
25 methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene, 2-amino-4-( $\beta$ -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol,  $\alpha$ -naphthol,  
30 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and the addition salts thereof with an acid.

35 When they are present, these couplers preferably represent from 0.0001 to 10% by weight approximately relative to the total weight of the ready-to-use dye

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composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The dye composition of the invention can also contain, in addition to the oxidation dye precursors defined above and the optional combined couplers, direct dyes to enrich the shades with glints. These direct dyes can then be chosen in particular from nitro dyes, azo dyes or anthraquinone dyes.

The subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, after which the fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 and 60 minutes and even more precisely between 5 and 40 minutes.

According to one specific embodiment of the invention, the process includes a first step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation base and optionally at least one coupler as defined above, and, on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one aminosilicone, and then in mixing them together at the time of use, before applying this mixture to the keratin fibres.

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Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices can be equipped with means for applying the desired mixture to the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

The first step (i) of this process consists in applying a reducing composition to the hair. This application is carried out lock by lock or all at once.

The usual step for placing the hair under tension  
35 in a shape corresponding to the desired final shape for  
this hair (for example curls) can be carried out by any  
suitable means, in particular mechanical means, which are  
suitable and known per se for maintaining the hair under

The hair can also be shaped without the aid of external means, simply with the fingers.

The oxidizing composition according to the invention can also be used in a process for bleaching keratin fibres, and in particular the hair.



Conventionally, a second step of the bleaching process according to the invention is a step of rinsing the keratin fibres.

The medium which is suitable for the keratin fibres (or the support) for the ready-to-use dye compositions and for the oxidizing compositions used for the permanent reshaping or bleaching of keratin fibres in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent in order to dissolve the compounds which would not be sufficiently soluble in water. By way of organic solvent, mention may be made, for example, of C<sub>1</sub>-C<sub>4</sub> alkanols such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the ready-to-use dye compositions and of the oxidizing compositions used for the permanent reshaping or bleaching of the keratin fibres in accordance with the invention is chosen such that the enzymatic activity of the 2-electron oxidoreductase is not adversely affected. It is generally between 5 and 11 approximately, and preferably between 6.5 and 10 approximately. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents, mention may be made, by way of example, of inorganic or organic acids such as

10

$$\begin{array}{ccc} R_{22} & & R_{24} \\ & \diagdown & / \\ & N \cdot W \cdot N & \\ & / & \diagdown \\ R_{23} & & R_{25} \end{array} \quad (IX)$$

The ready-to-use dye compositions and the oxidizing compositions for the permanent reshaping or bleaching of keratin fibres in accordance with the invention can also contain various adjuvants used conventionally in compositions for dyeing, permanently reshaping or bleaching the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, enzymes other than the 2-electron oxidoreductases used in accordance with the invention, such as, for example, peroxidases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, film-forming agents, preserving agents and opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional complementary

The ready-to-use dye compositions and the oxidizing compositions used for the permanent reshaping or bleaching of keratin fibres in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which are optionally pressurized, or in any other form which is suitable for dyeing, permanently reshaping or bleaching keratin fibres, and in particular human hair.

Concrete examples illustrating the invention will  
20 now be given.

The examples which follow illustrate the  
25 invention without being limiting in nature.

Example 1 of dye composition:

The ready-to-use dye composition below was prepared (contents in grams):

- 5
- Uricase from *Arthrobacter globiformis* at a concentration of 20 International Units (I.U.)/mg, sold by the company Sigma 1.5 g
  - Uric acid 1.5 g
  - para-Phenylenediamine 0.324 g
  - Resorcinol 0.33 g
  - 10 - Polydimethylsiloxane containing amino-ethylaminopropyl groups, at a concentration of 35% in water, sold under the name Dow Corning 939 Emulsion 1.2 g
  - Demineralized water qs 100 g

15 The ready-to-use dye composition described above was applied to locks of natural grey hair containing 90% white hairs for 30 minutes. The hair was then rinsed, washed with a standard shampoo and then dried.

20 Locks of hair dyed a matt dark-blonde colour were obtained.

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**Example 2:**      Oxidizing composition for permanent-waving  
or bleaching

- Uricase from *Arthrobacter globiformis* at a  
concentration of 20 International Units  
(I.U.)/mg, sold by the company Sigma      1.8 g
- 5 - Uric acid      1.65 g
- Ethanol      20.0 g
- (C<sub>8</sub>-C<sub>10</sub>)alkyl polyglucoside as an aqueous  
solution containing 60% active material  
(A.M.), sold under the name Oramix CG110 by 8.0 g  
the company SEPPIC
- Mixture of polydimethylsiloxane containing  
aminoethylaminoisobutyl/polydimethyl-  
siloxane groups, sold under the trade name  
Dow Corning Q2 8220 Fluid      1.0 g
- 2-Methy-2-amino-1-propanol      qs pH 9.5
- 10 - Demineralized water      qs 100 g

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